

## Supporting Information

# Hydrophobically Modified Poly(acrylic acid) Coatings on Silicone Hydrogel Contact Lens

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Materials and Methods

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Supporting References

## S1. Polymer Synthesis

**Materials.** 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (CTA) was synthesized according to a procedure reported in the literature.<sup>1</sup> Azobisisobutyronitrile (AIBN, 98%) was purchased from Junsei (Tokyo, Japan) and purified by recrystallization in methanol. Acrylic acid (AA, 99%), 1-decanol (98%), *N,N'*-dicyclohexylcarbodiimide (DCC, 99%), and 4-(dimethylamino)pyridine (DMAP, >99%) were purchased from Sigma-Aldrich (St. Louis, MO). Hexyl acrylate (HA, 96%), octyl acrylate (OA, 99%), and dodecyl acrylate (DDA, >98%) were purchased by TCI (Tokyo, Japan). All acrylate monomers were purified by passing through a basic alumina column to remove inhibitors before polymerization. HPLC grade toluene (>99.9%) was purchased from Burdick & Jackson (Morristown, NJ), HPLC grade *N,N*-dimethylformamide (DMF, 99.8%) was purchased from Daejung (Seoul, Republic of Korea), HPLC grade dichloromethane (DCM, >99.9%) was purchased from Samchun (Seoul, Republic of Korea) and used as a synthesis and polymerization solvent after purification using a solvent purification system (C&T International, Suwon, Republic of Korea).

**Methods.** <sup>1</sup>H nuclear magnetic resonance (NMR) spectroscopy was performed on a Bruker Avance 400 MHz spectrometer (Billerica, MA) using CD<sub>3</sub>OD (methanol-*d*<sub>4</sub>) and D<sub>2</sub>O as the solvent at a concentration of 4.2 mg/mL. Differential scanning calorimetry (DSC) was performed on a DSC Q25 (TA Instruments, New Castle, DE) using a scan rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere.

**Synthesis of decyl acrylate.** Decyl acrylate (DA) was synthesized following the literature procedure.<sup>2</sup> To a solution of AA (13.0 g, 174 mmol) in anhydrous DCM (150 mL) in an ice bath, DCC (49.0 g, 185 mmol) was added portion-wise. The solution was stirred at 0 °C for 2 h. Then, 1-decanol (25.0 g, 158 mmol) and DMAP (1.90 g, 15.0 mmol) dissolved in anhydrous DCM (50.0 mL) were added dropwise to the mixture and stirred at RT for 12 h. After completion of the reaction, the resultant mixture was filtered to remove dicyclohexyl urea and evaporated under reduced pressure. The product was purified by column

chromatography (EA/hexane = 1/20 (v/v)) and dried in the vacuum oven overnight (31.0 g, 88.0 % yield).

**Figure S2** shows the  $^1\text{H}$  NMR spectrum of the resulting product.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.42 (dd,  $J = 17.3, 1.5$  Hz, 1H), 6.14 (dd,  $J = 17.3, 10.4$  Hz, 1H), 5.83 (dd,  $J = 10.4, 1.5$  Hz, 1H), 4.17 (t,  $J = 6.7$  Hz, 2H), 1.74 – 1.62 (m, 2H), 1.46 – 1.22 (m, 14H), 0.90 (t,  $J = 6.7$  Hz, 3H).

**RAFT copolymerization of P(AA-co-DDA).** Synthetic procedure for P(AA<sub>184</sub>-co-DDA<sub>9</sub>) with  $i_{\text{DDA}} = 5\%$  is given as an example. A homogeneous solution of AA (0.940 g, 13.0 mmol), DDA (0.160 g, 0.690 mmol), CTA (25.0 mg, 69.0  $\mu\text{mol}$ ), and AIBN (0.0011 g, 6.9  $\mu\text{mol}$ ) was prepared in DMF (1.00 mL). The mixture was then transferred into an ampoule, degassed via three cycles of freeze-pump-thaw, and flame-sealed under vacuum. After heating at 60 °C for 12 h, the ampoule was cooled to room temperature and then opened to stop the polymerization. The mixture was dissolved in methanol and purified by removing residual monomers and impurities using precipitation in DCM. The product was obtained by evaporating the solvent under reduced pressure (0.900 g, 80.0 % yield).

All the other polymers with different compositions and molecular weights were synthesized by varying the [AA]:[xA]:[CTA] composition in the feed. **Table 1** summarizes the characterization details of the synthesized polymers in this study. Degree of polymerization ( $N$ ) was calculated based on the conversion of each monomer determined by  $^1\text{H}$  NMR spectroscopy. The DDA molar fraction ( $i_{\text{DDA}}$ ) was estimated by integrating the  $^1\text{H}$  NMR spectra of the polymer products.

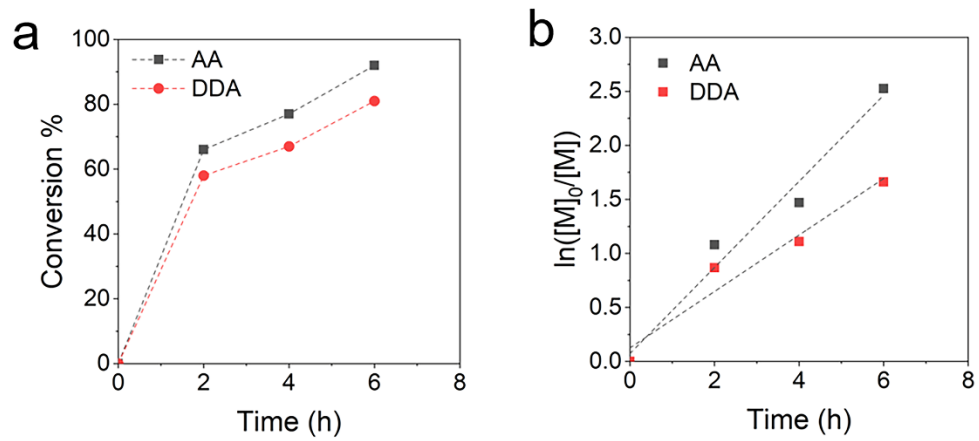
**Free radical copolymerization of P(AA-co-xA).** Synthetic procedure for P(AA<sub>2648</sub>-co-OA<sub>84</sub>) with  $i_{\text{DDA}} = 3\%$  is given as an example. A homogeneous solution of AA (12.8 g, 177 mmol), OA (1.00 g, 5.50 mmol), and AIBN (0.0100 g, 61.0  $\mu\text{mol}$ ) was prepared in DMF (15.0 mL). The identical freeze-pump-thaw cycles and workup procedures described above were employed to produce the polymer product (10.8 g, 78.0 % yield). All P(AA-co-xA)s with different molecular weights and compositions were synthesized

by varying the [AA]:[xA]:[AIBN] ratio. **Figure S3** shows the  $^1\text{H}$  NMR spectra of the resulting polymers.

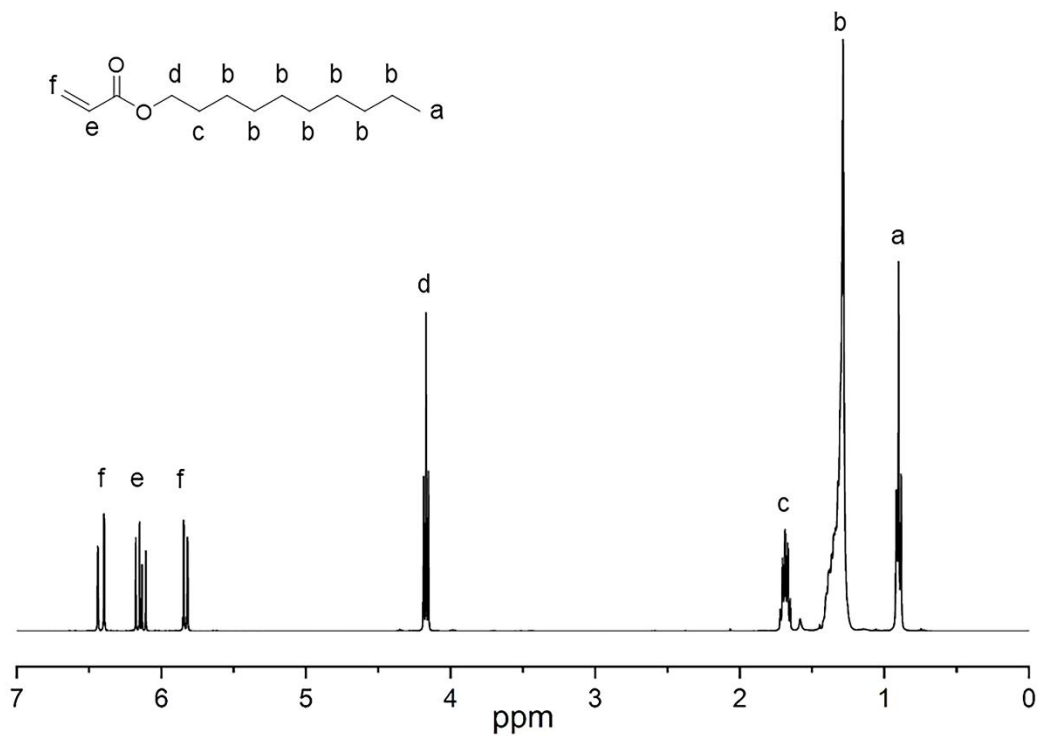
**Table 2** summarizes their characterization data.

**Calculation of Hydrophilic-Lipophilic Balance (HLB).** HLB was calculated by Griffin's method<sup>3</sup> using Equation (1), which accounts for the mass fraction of the hydrophilic part (AA) in the whole polymer:

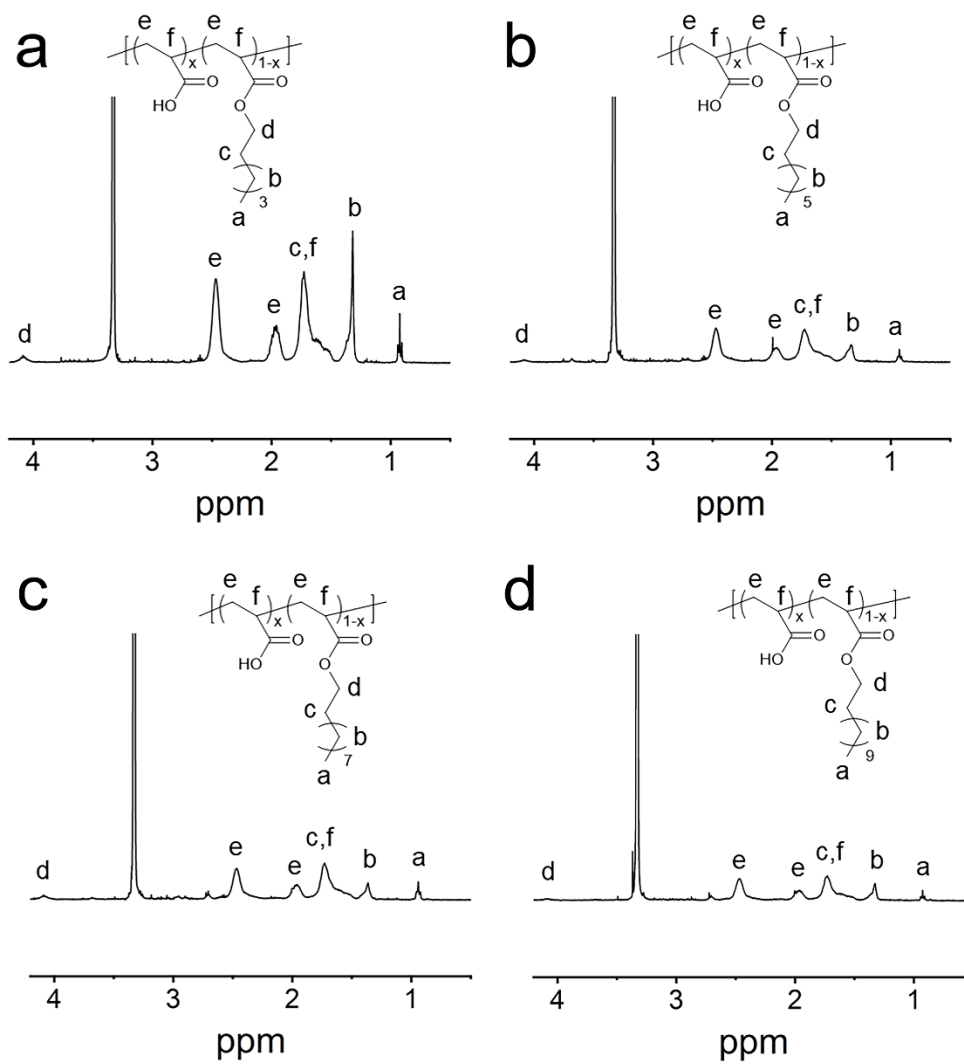
$$HLB = 20 \times \frac{\text{Mass of the hydrophilic part of AA}}{\text{Total mass of the surfactant}} \quad (1)$$



**Figure S1.** Copolymerization kinetics of AA with DDA. (a) Conversion over time. (b) First-order kinetics plot.



**Figure S2.** <sup>1</sup>H NMR spectrum of DA (400 MHz, CDCl<sub>3</sub>, 20 °C).



**Figure S3.**  $^1\text{H}$  NMR spectra of P(AA-co-xA)s (400 MHz,  $\text{CD}_3\text{OD}$ , 20  $^\circ\text{C}$ ). (a) P(AA-co-HA). (b) P(AA-co-OA). (c) P(AA-co-DA). (d) P(AA-co-DDA).

## S2. Polymer Characterizations in Aqueous Solutions and Coatings

**Solution preparation.** Homogeneous aqueous solutions of all polymers were prepared in deionized water at a concentration of 0.05 % by polymer weight. The solutions were mixed on a vortex machine for 5 min, sonicated for 1 h, and kept at 60 °C overnight.

**Coating of polymer solutions on Si wafer.** Silicon wafers were diced into 1 cm × 1 cm pieces for atomic force microscopy (AFM) analysis and 2 cm × 2 cm pieces for contact-angle measurements. Before polymer coating, each wafer was cleaned and hydrophilized using an RCA-based cleaning process. The wafers were immersed in an aqueous solution of NH<sub>4</sub>OH/H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O = 1/1/5 (v/v/v) at 80 °C for 10 min, followed by thorough rinsing with deionized water and drying under a nitrogen stream.

Aqueous polymer solutions were prepared at 0.05 wt% and filtered through a 0.45 μm PTFE syringe filter before use. The cleaned wafers were placed on a leveled surface, and 50–100 μL of the polymer solution was deposited onto each wafer by drop casting. The films were allowed to spread and dry under ambient conditions (20 – 25 °C) until no visible water remained. Samples were stored in a dust-free container prior to measurements.

**Coating of polymer solutions on lens.** Flat Si-Hy lens substrates with identical composition to the commercial lenses were used for surface characterization to eliminate curvature effects. The Si-Hy contact lenses were immersed in 95% ethanol at 25 °C for 3 h as a pretreatment step. The lenses were then rinsed with deionized water at 25 °C for 30 min. Subsequently, the P(AA-*co*-xA)s coating solution was applied at 25 °C for 1 h. After the coating step, the lenses were immersed in an aqueous surfactant solution at 25 °C for 1.5 h, followed by a final rinse with deionized water at 25 °C for 30 min. The surfactant treatment and rinsing steps are designed to remove loosely adsorbed polymer, leaving only stably associated polymer on the lens surface. The coating process is schematically presented in **Figure S8**.

**Contact angle measurements.** Static contact angles were measured using a contact angle goniometer (Phoenix 300, SEO, Republic of Korea). Droplets of deionized water, glycerol, and diiodomethane (DIM) were gently deposited onto the polymer-coated substrates using a microsyringe, and the droplet profiles were recorded immediately after deposition. All measurements were performed at room temperature.

The contact angles were determined by fitting the droplet shape to the Young–Laplace equation using the instrument’s analysis software. For each liquid, contact angles were measured at a minimum of three different positions on the sample, and averaged values were reported.

**AFM imaging.** AFM measurements were performed using a Bruker Dimension Icon scanning probe microscope. All images were acquired in PeakForce Tapping mode under ambient conditions. A SCANASYST-AIR-HPI silicon cantilever was used for imaging, with a nominal tip radius of ~2 nm, a nominal spring constant of 0.25 N m<sup>-1</sup>, and a resonance frequency of approximately 55 kHz. Height images were collected to analyze surface topography and local mechanical/compositional contrast, respectively. For quantitative roughness analysis, height images were plane-leveled and flattened prior to calculation of root-mean-square (RMS) roughness. Scan sizes and z-axis ranges are specified in the corresponding figure captions.

**Surface energy calculation.** The surface energy of the polymer-coated silicon wafers was calculated using the Owens–Wendt method based on static contact-angle measurements with two probe liquids of known surface-tension components: DIM and glycerol. The Owens–Wendt equation is given by:

$$\gamma_L(1 + \cos \theta) = 2 \left( \sqrt{\gamma_s^d \gamma_L^d} + \sqrt{\gamma_s^p \gamma_L^p} \right) \quad (2)$$

where  $\gamma_L$  is the surface tension of the liquid,  $\theta$  is the measured contact angle, and  $\gamma_s^d$  and  $\gamma_s^p$  are the dispersive and polar components of the solid surface energy, respectively. By solving the equation using

contact angles obtained with two liquids,  $\gamma_s^d$  and  $\gamma_s^p$  were determined, and the total surface energy was calculated as  $\gamma_s = \gamma_s^d + \gamma_s^p$ . The surface-tension values of the probe liquids were taken from literature.<sup>4,5</sup>

**Surface tension measurement.** The surface tension of the polymer aqueous solutions at the air–water interface was measured using a custom-built pendant drop apparatus. Polymer solution droplets were formed at the tip of a stainless-steel needle and allowed to reach a stable pendant shape under gravity. All measurements were performed at room temperature. The obtained droplet profiles were analyzed using Surfaceware software based on an axisymmetric drop shape analysis (ADSA) fitting to the Young–Laplace equation, using independently measured density differences ( $\Delta\rho$ ) for each polymer solution. For each sample, at least three independent droplets were measured, and the averaged value was reported.

**Viscosity measurements.** The viscosity of the solution was measured at 20 °C using a microVISC (HVROC-S) from RheoSense (San Ramon, CA).

**<sup>1</sup>H NMR relaxation time measurements.** Longitudinal ( $T_1$ ) and transverse ( $T_2$ ) relaxation times of the copolymers were measured using a Bruker AVANCE NEO 500 MHz (11.74 T) NMR spectrometer equipped with a Triple resonance broadband observe (TBO) probe. Polymer samples were dissolved in CD<sub>3</sub>OD at concentrations of 10 – 20 mg/mL, and all measurements were performed at 298 K.

**$T_1$  measurements.**  $T_1$  relaxation times were determined using an inversion–recovery (IR) pulse sequence ( $\pi$ – $\tau$ – $\pi/2$ ) with a series of variable delay times ( $\tau$ ). The recovery curves were fitted by area integration using TopSpin and analyzed with the monoexponential equation:

$$I(\tau) = I_\infty - A \exp\left(-\frac{\tau}{T_1}\right) \quad (3)$$

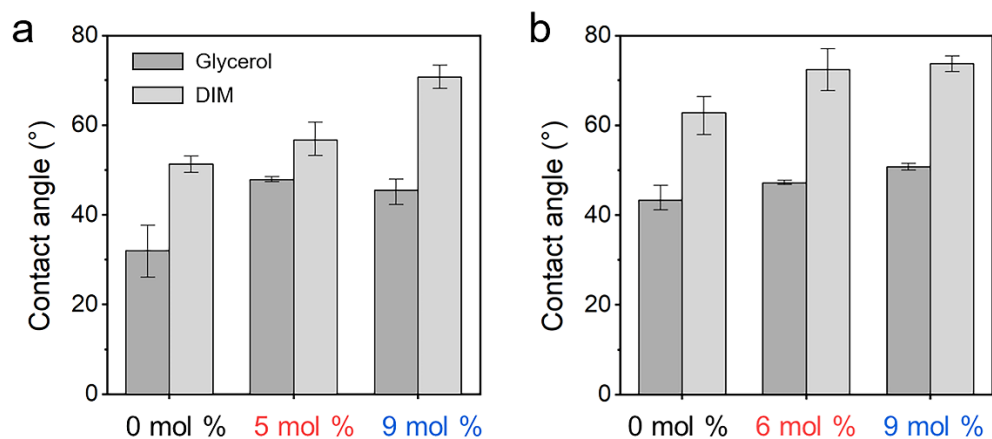
The fitted  $T_1$  values showed excellent agreement with monoexponential recovery behavior ( $R^2 > 0.99$ ).

**T<sub>2</sub> measurements.** T<sub>2</sub> values were obtained using a standard CPMG (Carr–Purcell–Meiboom–Gill) pulse sequence with variable total echo times (*t*). The signal decay was processed by peak-area integration using TopSpin (Bruker) software and fitted to a monoexponential model:

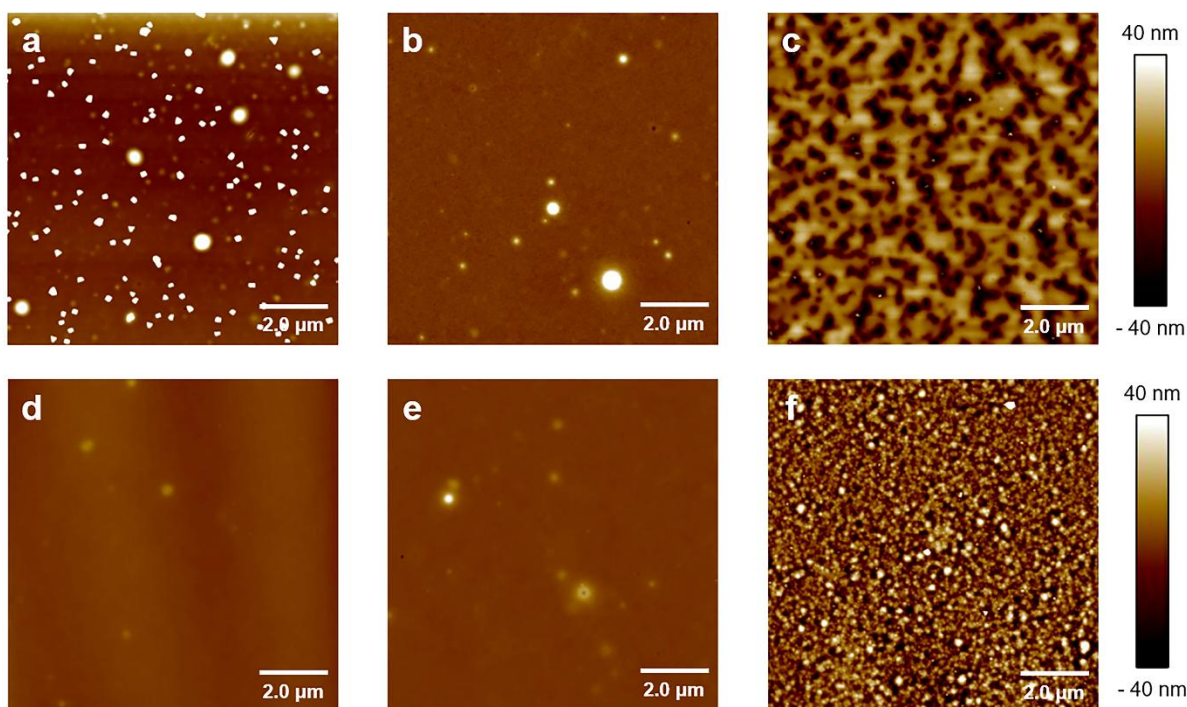
$$I(t) = A \exp\left(-\frac{t}{T_2}\right) + I_\infty \quad (4)$$

Only fits with R<sup>2</sup> > 0.99 were accepted for analysis.

**Friction coefficient measurements.** Friction coefficients were measured using a friction tester (STEP 100, ANTON Paar, Austria) equipped with a ruby ball probe. The measurements were performed under a normal load of 2 mN in phosphate buffered saline (PBS) solutions at room temperature. For each measurement, the tester cup was filled with PBS, and the contact lens was placed on the sample plate. The ruby ball was brought into contact with the lens surface, and the friction coefficient was recorded under a constant sliding motion at a sliding speed of 2 mm/s for 100 cycles. Each sample was measured at least three times, and the averaged values were reported.



**Figure S4.** Contact angles of glycerol and DIM on P(AA-co-DDA)-coated Si wafers with varying DDA contents. (a)  $M_{n,theo} = 25\text{--}34$  kg/mol. (b)  $M_{n,theo} = 14\text{--}17$  kg/mol.



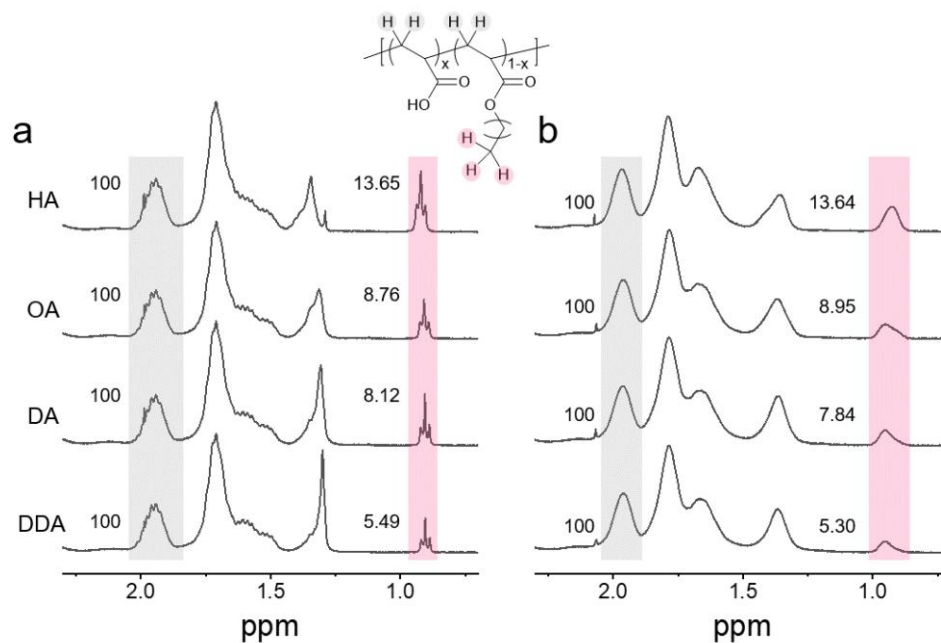
**Figure S5.** AFM height images of P(AA-co-DDA) coatings on Si wafers. Scan size:  $10 \times 10 \mu\text{m}^2$ ; Z-range:  $-40$  to  $40$  nm. (a) PAA<sub>190</sub> ( $i_{\text{DDA}} = 0\%$ ). (b) P(AA<sub>184</sub>-co-DDA<sub>9</sub>) ( $i_{\text{DDA}} = 6\%$ ). (c) P(AA<sub>176</sub>-co-DDA<sub>17</sub>) ( $i_{\text{DDA}} = 9\%$ ). (d) PAA<sub>344</sub> ( $i_{\text{DDA}} = 0\%$ ). (e) P(AA<sub>353</sub>-co-DDA<sub>20</sub>) ( $i_{\text{DDA}} = 5\%$ ). (f) P(AA<sub>346</sub>-co-DDA<sub>40</sub>) ( $i_{\text{DDA}} = 9\%$ ).

**Table S1.** RMS roughness of P(AA-*co*-DDA) coatings on Si wafers

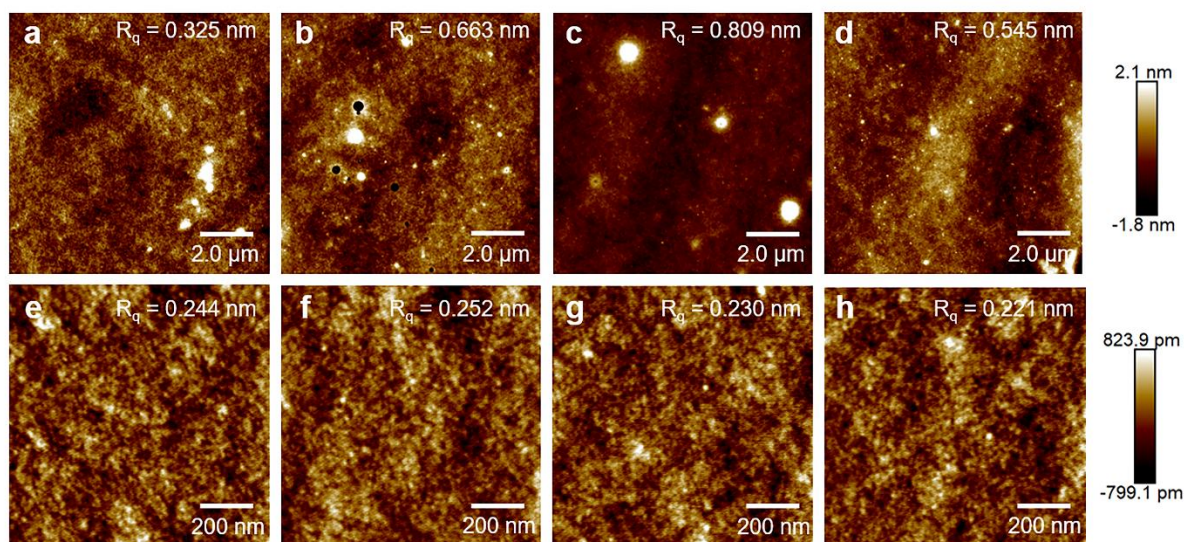
Sample name	$M_{n,theo}$ (kg/mol)	$i_{DDA,theo}$ (mol %)	RMS roughness (nm)
PAA <sub>190</sub>	14	0	14.9
P(AA <sub>184-<i>co</i>-DDA<sub>9</sub></sub> )	15	4	5.4
P(AA <sub>176-<i>co</i>-DDA<sub>17</sub></sub> )	17	9	13.2
PAA <sub>344</sub>	25	0	1.5
P(AA <sub>353-<i>co</i>-DDA<sub>20</sub></sub> )	30	5	1.5
P(AA <sub>346-<i>co</i>-DDA<sub>40</sub></sub> )	34	11	12.6

**Table S2.**  $T_1$  and  $T_2$  relaxation times of the alkyl and backbone protons in P(AA-*co*-*x*A)

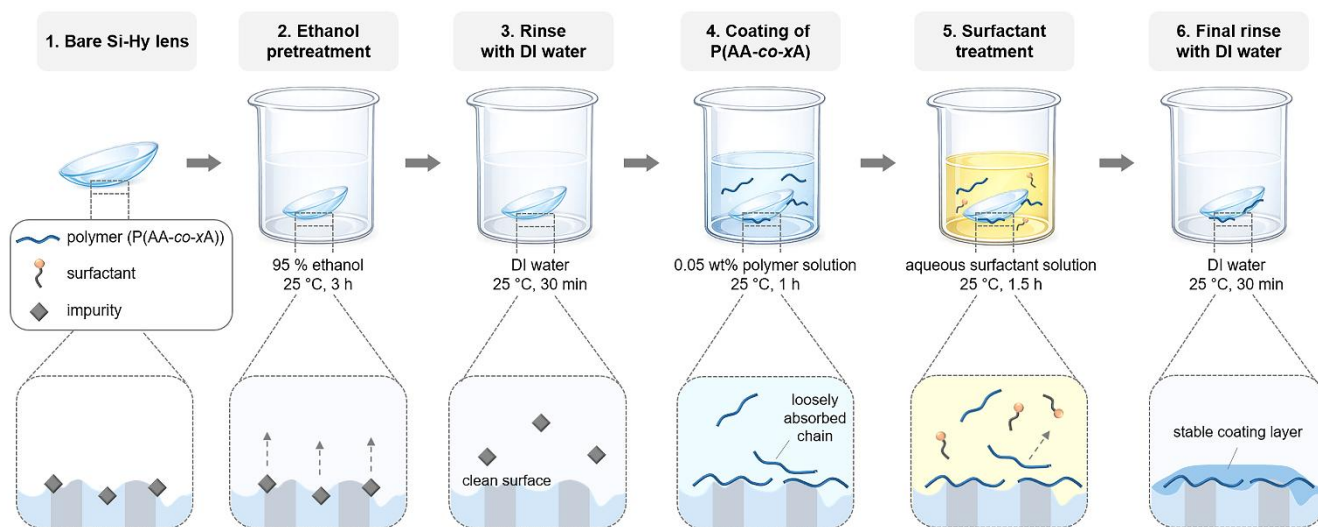
<i>x</i> A	peak	ppm	$T_1$ (s)	$T_2$ (s)	$T_1/T_2$
HA	alkyl CH <sub>2</sub>	1.459 – 1.302	1.134	0.847	1.339
	backbone	2.562 – 2.280	0.897	0.126	7.123
OA	alkyl CH <sub>2</sub>	1.448 – 1.276	1.071	0.744	1.439
	backbone	2.570 – 2.295	0.884	0.120	7.349
DA	alkyl CH <sub>2</sub>	1.465 – 1.185	1.020	0.732	1.394
	backbone	2.548 – 2.305	0.719	0.138	5.198
DDA	alkyl CH <sub>2</sub>	1.440 - 1.280	0.988	0.635	1.557
	backbone	2.552 – 2.296	0.565	0.052	10.770



**Figure S6.**  $^1\text{H}$  NMR spectra of P(AA-co-xA) copolymers in  $\text{CD}_3\text{OD}$  (a) and  $\text{D}_2\text{O}$  (b). The integral values of the backbone (grey) and the alkyl (pink) protons used for the relaxation time measurements are given next to the peak.



**Figure S7.** Large-area (a-d) and zoomed-in (e-h) AFM height images of P(AA-co-xA) coatings on Si wafers. (a, e) HA. (b, f) OA. (c, g) DA. (d, h) DDA. RMS roughness values ( $R_q$ ) are indicated in each image.



**Figure S8.** Schematic illustration of the coating procedure.

**Table S3.** Contact angle and friction coefficient of P(AA-co-xA)-coated lenses

	$M_{n,theo}$ (kg/mol) <sup>a</sup>	Contact angle (°)	Friction coefficient <sup>b</sup>
Bare lens (Dk100)	-	76.4	-
P(AA <sub>1166</sub> -co-HA <sub>48</sub> )	89	86.8	0.029
P(AA <sub>1324</sub> -co-OA <sub>42</sub> )	103	42.8	0.028
P(AA <sub>1316</sub> -co-DA <sub>35</sub> )	105	74.4	0.030
P(AA <sub>1220</sub> -co-DDA <sub>30</sub> )	95	71.0	-

<sup>a</sup>Not applicable for the bare lens.

<sup>b</sup>-: Could not be determined reliably.

### S3. References

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